# CHAPTER 11

ESSENTIAL OILS AND ESSENCES

Citrus peel contains oblate-shaped oil glands in the flavedo, which extend to different depths into the albedo of all citrus fruits. These cells contain chemicals discharged by metabolic processes of the fruit, which give each type of citrus its characteristic aroma and flavor. The prominent chemical classes present in these oils are terpenes, and the hydrocarbon, d-limonene, is the major constituent. The character of the flavor is mostly dependent on oxygenated terpene derivatives, aldehydes, ketones, esters, alcohols, and acids of the oils. The value of these oils for food and beverage flavorings, perfumery, and chemical uses has long been recognized. The large volume of published information and scientific literature about citrus essential oils are impractical to discuss in a single chapter. Therefore, the emphasis here will be related to the important technological issues of oil recovery, composition and properties, process variables, and products.

11.1 RECOVERY

The attentive student may find documentation of the early history of citrus oil recovery in many sources. Commercial quantities of lemon oil were made for centuries in the Motherland of essential oils (Sicily) by pressing peel in wooden screw presses or by hand squeezing oil-saturated sponges touched against scarified fruit. Classic essential oil reference volumes describe these processes and characterize the oils from citrus (Guenther, 1949). Early commercial sweet-orange oil recovery in the United States by the hand-sponge technique, vacuum distillation of aqueous extracts, and by pressing water-extracted peel has been

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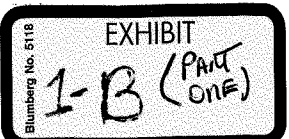
described (Hood and Russell, 1916). Later publications described citrus oil recovery, mechanical techniques, and oil properties (Kesterson and McDuff, 1948; Braverman, 1949; Kesterson et al., 1971).

11.1.1 Extraction

Current citrus industry recovery involves oil extraction machinery associated with the specific type of juice extractor in use. With a few exceptions, peel oil extraction is concurrent with the FMC, Brown, or Italian juice extractor systems (Chapter 4). Good descriptions of these oil extraction systems and information about the technology and machinery used has been reviewed (Huet, 1991). Universally, water is the solvent or carrier for the peel oil as it is extracted from the oil glands and enters the recovery process. Since the oil components are mostly insoluble in water, recovery involves handling oil–water emulsions and homogeneous suspensions (Matthews and Braddock, 1987). For efficiency, modern processes recycle the water within the oil recovery systems.

11.1.1.1 FMC Process The FMC oil recovery procedure is unique because the juice extractor contains the components necessary to rupture the oil glands and extract the oil into the emulsion. This process minimizes the space and energy for high yields of oil from the peel, at the same time extracting the juice (FMC, 1998). Oil extraction occurs in sequence after fruit is placed on the lower extractor cups and cutter tubes, the upper cups descend, and plugs are cut in the fruit from the bottom cups. The upper cups descend, forcing the juice and inner fruit contents down through the bottom tube for juice recovery. At the same time, the peel is shredded, being forced through openings in the upper cups, which ruptures the oil glands. The upper cups contain spray rings, which apply pressurized water to the peel during and after the shredding step, emulsifying the oil as it is released. This emulsion and small particles of peel and soluble and insoluble solids flow from the extractor, are collected, and sent to a finisher for initial separation of the larger particles. The finished emulsion is sent to a centrifugation process for concentration and recovery of the final cold-pressed oil. The water discharge from the centrifuges is filtered and recycled to the process.

Process variables may affect oil yield and quality. Generally, fruit size, condition, and quality are of major importance, where firm, mature fruit that fits properly into the extractor cups produces highest oil yields. Enough water also must be sprayed onto the shredded peel to adequately carry the emulsion, but not so much that emulsion oil concentration will require extensive centrifugation to recover the oil. The amount of water used in the extraction process generally does not affect the oil quality (aldehydes) as much as the fruit maturity (Steger, 1981). Peel sugars dissolve in the water during recycling and may concentrate to the range of 4–10 °Brix, before bleed-off to the feed mill waste stream. Good sanitation is a requirement for recycle systems since the incoming fruit provides inoculum for microbial growth on the sugars, which

in turn can result in fermented flavors in the cold-pressed oil. Water use for orange peel oil recovery may average 10–11 L/box (3 gal/box) at >50% oil recovery extraction efficiencies of the amount in the fruit (Steger, 1979). Some amount of water is absorbed by contact with the peel in this process and must be evaporated in the feed mill.

11.1.1.2 Brown Oil Extractor (BOE) and Shaver

The Brown juice extraction process (Chapter 4) maintains two oil extraction systems, the peel shaver and the BOE. The shaver has largely been replaced by the BOE, but is still available for certain by-product applications and for tangerine oil extraction, after juice recovery with Brown 700 or 1100 extractors (Chapter 4). This machine operates by shaving the flavedo from the albedo of the peel from the extractors, spraying water onto the flavedo as it is pressed between knurled rolls, releasing the oil into the water to obtain the emulsion. The knives may be set to different thickness for degree of flavedo shaving into the albedo layer. Separate by-product streams of flavedo and albedo may be obtained in addition to the oil emulsion. Optimal shaver setup involves placing a machine beneath each juice extractor.

The BOE operation requires the machine to be installed in the fruit stream after washing and before the juice extractors. This machine extracts the oil by passing fruit over a series of rotating toothed rollers in a pool of water (Bushman, 1972). The oil glands are cut, releasing the oil into the water, and the fruit passes on to the juice extractor. Although this is a scarification process, very close inspection of the fruit surface is required to detect the cuts. An improvement, allowing movement of blocks of fruit at a time, is claimed to increase oil yield (McKinney, 1981).

Water is typically recycled, reducing water usage, to a °Brix where bleed to the feed mill occurs. Because only the flavedo is contacted by water, the peel does not absorb much water and the emulsion water °Brix increases slowly during recycling, resulting in low viscosity of the stream feeding the centrifuges. In a recycle system, the BOE process will require 1–4 L/box (0.3–1 gal/box) makeup water added as a fruit rinse at the end of the process (Waters, 1993). Low amounts of insoluble solids in the emulsion stream increase oil recovery efficiencies in the centrifugation steps. The BOE may be set up for efficient oil extraction from the different fruit varieties, reducing peel oil concentration in the juice during extraction, provided the fruit surface is adequately rinsed after oil extraction. A necessary requirement for efficient operation of this machine is to prevent fruit rate overload; otherwise, the surface will not contact the rollers and release the oil. A complete description of this process and its operation to recover >50% of the oil in Valencia oranges has been published (Waters, 1993).

11.1.1.3 Italian Machines

Some peel oil is recovered from whole fruit by a scarification process, whereby whole fruit enter a cylindrical chamber containing spinning sharp perforated rollers. As the fruit pass down through

the machine, the flavedo is scarified, releasing the oil into a water spray inside the chamber. The oil–water emulsion collects in the bottom and is sent to the finishing/centrifugation process, while the fruit proceeds on to the juice extractors (Chapter 4). An alternate process extracts oil from peels of half fruit (or whole fruit, including the juice) by mixing with water in a screw press. The press liquid is the oil emulsion stream, and the press cake may be mixed with more water and pressed again to increase yield. This emulsion may be centrifuged for cold-pressed oil recovery or sometimes, distilled to recover the oil. These processes produce oils high in pigment, wax, and residue, and they have specific demands by the flavor industry, different from oils extracted by the Brown or FMC processes.

11.1.2 Centrifugation

Following a finishing step to remove larger insoluble pieces of peel, cold-pressed oil recovery from emulsions of the extraction processes involves a two-stage centrifugation process. Operation of the entire process may be automated, and efficiency of the extraction/centrifugation process determines the oil yield; however, the primary efficiency limiting step is the extraction from the peel. In some cases (tangerine oil), the finishing may involve heating the peel/oil emulsion in the finisher. This helps extract oil from the peel particles and increases centrifuge efficiencies due to lower viscosity of the hot emulsion. The process is defined in the flow diagram of Figure 11.1, showing the initial oil concentration in the emulsion, 0.5–3.0%, is concentrated to 50–70% by the separator. The concentrated emulsion is fed to the polisher and separated into pure oil and a waste sludge. The first-stage separator, known as the desludger, may operate between 7000 and 10,000 times gravity at 100–400 L/min (25–100 gal/min), while the much smaller polisher operates at similar g forces at lower feed rates of 5–10 L/min (1.3–3 gal/min) (Matthews and Braddock, 1987).

The maximum oil recovery efficiency depends on each operation since the overall efficiency is a multiple of the efficiency of each process. Excellent discussions of the variables relating yield, extraction, and centrifugation of peel oil emulsions to process efficiency has been published for the BOE and shaver (Waters, 1993) and for the FMC process (Ferguson, 1980). In general, the simplest calculation of efficiency works for each of these processes, as follows:

Total process efficiency (eff) = (extraction eff) $\times$ (separator eff) $\times$ (polisher eff)

Extraction eff(%) = 100(MO)/WF

Separator eff(%) = 100(F − AQ)/F

Polisher eff(%) = 100(CE − S)/[CE − ($S \times$ CE/100)]

where MO is the mass oil in extracted dilute emulsion, WF is the mass oil in whole fruit, F is the percent oil in feed stream, AQ is the percent oil in aqueous

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WATER ──→ OIL EXTRACTION ◄──┐
                │           │
                ▼           │
PEEL    ◄── FINISH          │
PIECES                      │
                │           │
                ▼           │
            EMULSION        │
            0.5 - 3.0 %     │
                │           │
                ▼           │
                          AQUEOUS
SLUDGE ◄── SEPARATOR ──→ DISCHARGE
                │
                ▼
            CONCENTRATED
            EMULSION
            50 - 70 % OIL
                │
                ▼
            POLISHER ──→ SLUDGE
                │
                ▼
               OIL
                │
                ▼
            DEWAX ──→ WAX
                │
                ▼
            COLD-PRESSED OIL
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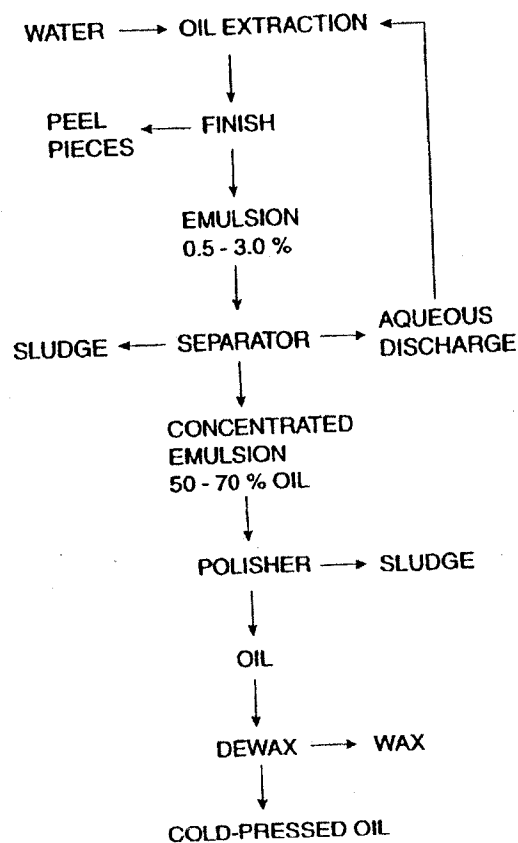
Figure 11.1 Flow diagram of a typical citrus cold-pressed oil recovery and water recycling process.

discharge, CE is the percent oil in concentrated emulsion from separator, and S is the percent oil in sludge.

The extraction efficiency is not simple to calculate without some guessing for the various extraction processes. For all methods, fruit flow must be estimated, but other than the BOE, oil in the various component fractions must be determined, as well as an estimate of their mass flow rates. Under ideal conditions, it should be possible to extract 60–75% of the oil from the fruit and to actually recover 95% of the amount extracted. Picking, hauling, loading, and unloading fruit causes loss of oil cell turgor and subsequently lowers oil recover compared with fruit fresh from the tree. Also, economic value may help determine process efficiency. One would tend to try harder to recover lemon oil than orange oil. However, these calculations help monitor equipment operation performance, even with many variables affecting each process. Full understand-

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ing is required for optimum benefit and the bottom line is the amount of total oil in the fruit actually recovered.

11.1.3 Total Oil in Fruit

11.1.3.1 Quantity   Amounts of peel oil in the various citrus varieties were determined by early extaction procedures for lemon and orange oils. Hood and Russell (1916) reported that 3.5 kg oil/mt fruit (7 lb oil/ton) could be obtained from oranges by a scarification/pressing process. Also, ranges of 4–10 kg/mt (8–20 lb oil/ton) for California lemons and 2–4.5 kg/mt (4–9 lb/ton) Valencia oranges by both hand pressing–sponge and machine methods were reported (Poore, 1932). Theoretical values of the total oil available for recovery in the various commercial Florida citrus varieties have also been determined (Kesterson and Braddock, 1975). These values, presented in Table 11.1, support the historic and modern commercial 60–75% yields of oil in the fruit obtained by recent manufacturing processes. Examination of the results clearly shows that tangerines, Valencia oranges, and lemons have more peel oil than grapefruits, early–midseason oranges, Temples, and Persian limes.

11.1.3.2 Horticultural Variables   The importance of horticultural practices to crop yields and fruit and juice quality is recognized. However, there have not been many studies in relation to peel oil content and quality. Considering the surface of an individual fruit, more oil was found in the bottom (stylar) half and south-facing part of California Valencia oranges (Bartholomew and Sinclair, 1946). A comparison of peel oil content from over 30 Valencia budwood selections budded to one type of rootstock found values ranged from

TABLE 11.1   Peel Oil Content of the Major Citrus Cultivars

Cultivar	Samples[b]	Lb Oil/Ton Fruit[a]			
		Min.	Max.	Mean	SD
Hamlin	64	7.0	8.2	7.8	1.5
Pineapple	100	7.1	14.0	9.7	1.0
Valencia	255	10.4	16.3	13.5	1.8
Dancy tangerine	45	13.5	17.4	15.5	1.8
Temple	47	6.8	9.1	7.9	0.7
Orlando tangelo	36	9.7	12.7	11.3	0.7
Duncan grapefruit	83	4.8	6.9	5.6	0.6
Marsh grapefruit	87	5.5	7.3	6.2	0.5
Ruby grapefruit	82	5.1	7.8	6.5	0.5
Bearss lemon	270	11.9	19.2	15.1	2.4
Persian lime	121	7.3	9.2	8.1	1.2

[a]Multiply by 0.5 to convert lb/ton to kg/mt.
[b]Total samples for four seasons (Kesterson and Braddock, 1975).

5.5 to 8 kg/mt (11 to 16 lb/ton fruit). This study also reported that the same budwood scion on 19 rootstocks showed oil yield was also affected by the rootstock, although not to the degree as the budwood selection (Hendrickson et al., 1970). Budwood selected from clones with high fruit yields showed oil content increases of 2 kg/mt (4 lb/ton) of lemons and 2.3 kg/mt (4.6 lb/ton) of Valencia oranges, compared with the standard varieties (Kesterson and Braddock, 1977). Fertilization studies on lemons and pineapple oranges have also demonstrated that increased nitrogen increased oil yield, while increased application of potassium suppressed oil yield (Kesterson and Braddock, 1977; Kesterson et al., 1977). Statistically significant differences in shape, rind thickness, juice yield, acid content, and color were determined from lemons from 11 countries, illustrating the diversity of this fruit (McDonald and Hillebrand, 1980).

The aldehyde content of orange oil is a primary indicator of flavor strength, and higher is better. A study of the effect of fruit maturity on the chemical and physical properties of Valencia oil reported that oil from immature (green) fruit had 1.3% aldehydes and lacked fresh character, while oil from mature fruit had 1.8% aldehydes and good aroma (Kesterson and Hendrickson, 1962). Similar studies for grapefruits have reported that aldehydes and nootkatone contents increased until the fruit was past peak maturity (Kesterson et al., 1965). Citrus fruit at the peak of maturity and firmness should have the highest oil yield, at maximum turgidity of the oil glands. It is after this time the flavor and aldehyde contents of the oils are highest.

11.1.4 Juice Oil

Considerable peel oil may find its way to the juice during juice extraction. Since most consumers prefer juice to have less than 0.025–0.030% oil, excess oil is removed from NFC juices (Chapter 5) before packaging. Depending on fruit type and extractor setting, juice peel oil content after the extractors may be as high as 0.06% by volume in situations where maximum juice recovery is the objective. The NFC juice oil reduction to 0.020% may be done by extractor setting to less pressure conditions, or by vacuum/steam stripping part of the volatiles. Economically, lower extractor and finisher settings stipulate lower juice yields, and vacuum deoiling may lose desirable volatile flavors.

An older technology, which has seen revival since the advent of aseptic NFC juice, allows removal of excess juice oil by centrifugation. The many ways centrifuges can be used for pulp reduction, debittering, viscosity control, and the like in citrus plants have been documented (Distelkamp, 1962). A process scheme to recover juice oil by centrifugation claimed to produce a fresh-flavored juice and oil with much better top-notes than oil recovered by vacuum stripping of single-strength juice (Thrush, 1964). The centrifugation process to recover juice oil involves separation of a concentrated emulsion from the juice, where as much as 50–65%, v/v, oil reduction occurs. This concentrated emulsion may be clarified in a small polisher, similar to cold-pressed oil

recovery. The oil recovered may amount to as much as 65% of the volume of oil reduction of the juice stream. The properties of juice oil are very similar to essence oil from juice evaporators, where esters and top-notes predominate over aldehydes. Juice oil from oranges has been described to have less aldehydes and more esters than cold-pressed oil (Kesterson and Braddock, 1976).

11.1.5 Wax

The nonvolatile peel cuticular wax coating, pigments, lipids, flavonoids, and some suspended water and other matter dissolved in the oil during extraction is termed wax. The wax is perceived as a defect in cold-pressed oil, which has been chilled, as it crystallizes and the flocculant has an unsightly appearance. The composition of this wax has been described for lemons and oranges (Sinclair, 1984) and for grapefruits (Markley et al., 1937). The cuticular waxes are primarily long-chain hydrocarbons and alcohols of carbon chains between C_{20} and C_{26}. A thorough study of the wax constituents of grapefruit peel has identified the triterpenoid, friedelin, as a major constituent, including the alkanes, alcohols, sterols, and squalene (Nordby and McDonald, 1994). Grapefruit trees conditioned in 15°C chambers against chilling injury contained higher quantities of squalene in the wax, evidence that this compound may protect fruit from chilling injury (Nordby and McDonald, 1990).

The cold-pressed oil recovery process involves winterization to reduce the wax content. Besides being unsightly in the oil, which may be added to clear beverages, wax can cause viscosity problems during vacuum distillation (folding) to remove terpenes from the oil. The conditions for winterization have not been well defined; however, the wax crystallizes from oil held at temperatures below 0°C for long periods (Hendrix et al., 1992). The lower the temperature, the shorter the time needed for dewaxing. Cold-pressed oil may be typically chilled to −25 to −40°C from 2 days to a week and then filtered through diatomaceous earth to remove the wax. Higher temperature (−15°C) from 20 days to several months may be used without filter aid, where the oil is decanted. Grapefruit oil is usually winterized by holding for 3 weeks at −24°C, then recovered by filtration.

Oil in bulk quantities is held in slender, conical bottom, stainless steel tanks to facilitate decanting the clear oil above the precipitated wax (Matthews and Braddock, 1987). The chilling process and cold storage of the oil require refrigeration energy. To cool cold-pressed oil from ambient temperature of the centrifuge process across a temperature differential of 20–60°C would require 36–110 kJ/kg oil, or about 0.7–2.1 kWh, based on the specific heat of d-limonene (1.834 kJ/kg K) (Braddock and Miller, 1982).

11.2 COMPOSITION

There have been many studies of the composition of volatile constituents in the various citrus oils. The interested reader may examine the studies listed

TABLE 11.2 Approximate d-Limonene Concentration of Various Citrus Essential Oils

Product	Limonene (%, v/v)
Citrus terpenes, d-limonene[a]	>95
Orange, tangerine, tangelo[a]	95
Grapefruit[a]	93–95
Essence oil[a]	95
Lemon[a]	75–80
Lime, Mexican, Persian[a]	50–55
5-Fold orange, grapefruit[b]	90
10-Fold orange[b]	80–85
25-Fold orange[b]	60–65
36-Fold orange essence oil[a]	1–2

[a]Braddock et al. (1986).
[b]Vora et al. (1983).

here for reference and pursue the literature for in-depth information. A complete database of the individual composition and concentrations of the classes (hydrocarbons, carbonyls, etc.) of volatile compounds for most of the citrus oils and juices has been compiled (Maarse and Visscher, 1989). This useful work is now probably the standard for identity and quantity of the hundreds of volatile flavor components found in the individual citrus fruit. This database is complemented by a thorough review of the individual chemicals and chemical classes considered important to flavors from oranges, tangerines, mandarin fruits, grapefruits, lemons, limes, and kumquats (Shaw, 1991). Citrus oil composition of interest for commercial purposes involves physical and chemical properties as well as typical aroma and sensory evaluation. While oils from the various citrus cultivars have distinct aroma and flavor specific to their fruit source, these oils are surprising in their chemical similarity. The oils from the various oranges, grapefruits, tangerines, and hybrids have d-limonene contents greater than 90%, while lemon and lime oils may have less than 75% d-limonene (Table 11.2). All citrus oils contain over 90% monoterpenes, considering both d-limonene and oxygenated terpenes.

11.2.1 Orange Oil

The chemical and physical property standards of identity for cold-pressed orange oil are defined in individual monographs of the various citrus oils (Food Chemicals Codex, 1996). These standards (e.g., cold-pressed orange oil) establish analytical methods and ranges for specific gravity (0.842–0.846), refractive index (1.472–1.474), optical rotation (+94° to +99°), aldehyde content (1.2–2.5%), and heavy metals. Specific gravity, optical rotation, and refractive index

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of the oil are properties, measured historically, with the goal of adulteration detection. These values still find use in evaluation of oil properties for flavor emulsions and formulations related to specific oil characteristics. The flavor strength of the oil, estimated by measurement of the aldehyde content by quantitative wet chemistry, is also useful for economic reasons in the oil trade and for product formulation. Aldehyde contents of early and midseason orange oils are generally in the lower part of the Codex standard range, while Valencia oils are higher.

The aroma and flavor significance of the volatile compounds of the various orange oils as used in juices, beverages, and foods is undeniable. However, consider the challenge to flavor formulators using quantitative data of the individual components listed in the database (Maarse and Visscher, 1989). For example, 14 references in the orange peel oil database listed concentrations from 360 to 4000 ppm for the hydrocarbon, valencene, an important flavor component. Even more significant is the value range of 1700–22,000 ppm for decanal, a major aldehyde contributing to the total aldehyde content (by the Codex analysis). The Codex range of 1.2–2.5% total aldehydes would dictate that values below 10,000 ppm in the literature might be erroneous.

The importance of citrus oil oxygenated components have resulted in studies to better define quantitative composition of the oils. The major aldehydes of the oils are the homologous series of aliphatic C_2 units and terpene aldehydes, made by biochemical synthesis in the fruit. The concentrations of orange oil aldehydes were determined by chemical and crystallization methods as 31% octanal, 27% decanal, 6% dodecanal, and 7.5% citral (Naves, 1947). Decanal and octanal are the primary aldehydes of the citrus oils with the exception of lemon and lime oils, which contain citral (neral + geranial). Aldehyde content of commercial Florida oils, determined by quantitatively preparing the 2,4-DNPH derivatives is reported in Table 11.3 (Braddock and Kesterson, 1976).

TABLE 11.3 Concentration of Major Florida Citrus Oil Aldehydes as Dinitrophenylhydrazone (DNPH) Derivatives[a]

Oil	C_6	C_8	C_{10}	C_{12}	C_{14}	Neral	Geranial
Hamlin	1.2	29.2	22.7	15.1	6.1	1.1	9.3
Pineapple	0.5	28.2	18.0	9.9	6.5	6.9	10.1
Valencia	1.0	27.3	30.7	9.4	5.3	4.1	4.4
Valencia (Calif.)	Trace	20.0	37.2	9.8	4.0	5.8	7.4
Temple	Trace	32.2	17.9	10.7	5.4	3.6	4.5
Dancy tangerine	Trace	23.1	24.0	13.5	4.8	5.0	5.7
Orlando tangelo	Trace	26.0	23.6	12.2	10.1	9.0	6.0
Duncan grapefruit	Trace	29.9	17.8	12.7	6.9	2.1	7.1
Essence oil (Val.)	0.5	13.8	26.7	5.5	1.0	6.0	4.2

Header span: % (wt/wt) of Total Aldehydes

[a]Modified from Braddock and Kesterson (1976).

11.2.2 Tangerine (Mandarin) Oils

Since tangerine juice is less common than orange juice, fewer fruits are grown and processed, a requirement for recovering oil. Cold-pressed tangerine oil has the unique aroma of the mandarin fruits, different from orange, yet the composition of the major constituents is similar. The source of this aroma is in the minor constituents and compositional ratio of the major components, which have been reviewed (Lawrence, 1992). In different parts of the world, different mandarin cultivars are grown and each has a slightly distinct oil aroma. Of the oxygenated oil components responsible for this unique aroma, methyl-N-methylanthranilate, thymol and sesquiterpenes, α-sinensal, and β-sinensal are very important in the juice (Shaw, 1991, 1996) and in the oil (Moshonas and Shaw, 1974). Tangerine oils are also valued for their dark, reddish pigmentation, which is useful for blending natural color into certain beverage formulations.

11.2.3 Grapefruit Oil

Grapefruit flavor and aroma is quite unique and distinguishable from the other citrus varieties by being harsher and less easily affected by processing and storage (Shaw, 1991). Collected directly from the polisher, cold-pressed grapefruit oil lacks typical grapefruit aroma and, by odor, is difficult to distinguish from orange oil. Cold-pressed grapefruit oil flavor benefits from storage, or aging, to develop its distinctive grapefruit character. Also, except for color, there is little difference between white and red grapefruit oils. The oil is quite stable during storage for 6–12 months at 18°C, during which time the linalool content decreases and the full-bodied grapefruit aroma develops (Kesterson and Hendrickson, 1967). The stability during storage may be influenced by the high level of α-tocopherol (>250 ppm) in the cold-pressed oil, which is twice the amount in orange oil (Waters et al., 1976).

The grapefruit-like character of the oil and juice once was thought to be largely influenced by the compound (+)-nootkatone (Fig. 11.2) (Shaw, 1991). Many studies of the volatile juice constituents have established the difficulty of quantifying the highly volatile compounds (Cadwallader and Xu, 1994). However, studies by commercial researchers have defined the major character-impact components of grapefruit juice (and presumably, oil) to be terpene thiols. Identification of the compound, 1-p-menthene-8-thiol (Fig. 11.2) has resulted in the ability to synthetically reproduce the flavor of fresh grapefruit (Demole et al., 1982). Discovery that 1-p-menthene-8-thiol has an aroma threshold below 1 ppb makes this compound one of the most potent known natural aromas. A number of these thiols have been identified and synthesized by acid catalysis of terpenes with hydrogen sulfide (Janes et al., 1993). These compounds, as well as some sesquiterpenes (Demole and Enggist, 1983), similar to (+)-nootkatone, practically complete the definition of fresh grapefruit flavor. Mixtures of 1-p-menthene-8-thiol and α-terpineol added to β-
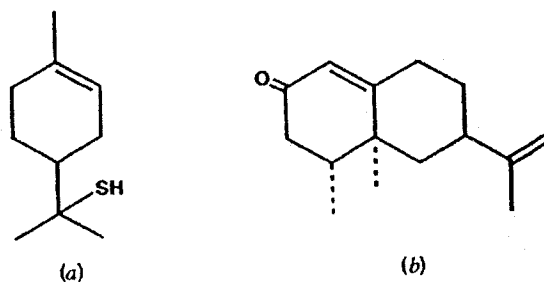
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(a)   *(b)*

Figure 11.2 Components important to the flavor of fresh grapefruit juice. (*a*) 1-*p*-menthene-8-thiol and (*b*) (+)-nootkatone.

phenylethanol have been shown to have different aroma characteristics at different concentrations. At 1–5 ppm, the mixture has a rose petal aroma, and at 10^{-5} ppm the material has a guava, grapefruit-like tropical note (Mookherjee et al., 1985).

11.2.4 Lemon and Lime Oils

Lemon and lime trees are more temperate than the other citrus varieties, which limits their distribution to the warmer world citrus zones. The trees have more thorns than oranges, which makes picking the fruit difficult. Also, the juice, because of its acidity, is not as marketable as orange juice, all factors contributing to fewer plantings of these fruits. Since the oils are very prized for their flavor and aroma, scarcity of fruit and low demand for processed juice results in higher value of these oils compared to the other citrus oils (Table 11.4).

The aldehyde content of lemon oil is considerably higher than orange, ranging from 2.0 to 5.5% (as citral) (Food Chemicals Codex, 1996), depending on the type of lemon and the growing locale. Lime oil aldehyde content is even higher, with differences noted between cold-pressed and distilled West Indian (Mexican) and Persian (Tahitian) limes (Table 11.5). The d-limonene content of these oils is also significantly less than that of the other citrus oils. Oil from a lemon cross, the Meyer lemon, has an unusual aroma related to its composition of approximately 5% thymol (Moshonas et al., 1972); however, this oil has a low aldehyde content. Cold-pressed lemon and lime oils also contain significant amounts of coumarin-type compounds in the high-boiling fraction. Some of these coumarins and psoralens may cause photosensitive skin reactions in people who come in contact with the oil and go into the sunlight. Based on concentration of coumarins, particularly bergapten, in the peel, Persian lime oil may be potentially more phototoxic than West Indian lime oil (Nigg et al., 1993).

The lime oil of commerce is distilled West Indian oil, which is manufactured by distillation of a water extract of peel or whole, chopped, pressed fruit.

TABLE 11.4 Approximate Value of 1 lb of Various Citrus Oils of Commerce[a]

Oil	$ Value
d-Limonene	0.45
Orange, Brazil Pera	0.65
Orange, FL midseason	0.70
Orange, FL Valencia	0.77
Orange, CA distilled	1.25
Orange, bitter	19.00
Grapefruit, FL	12.00
Tangerine, FL	14.00
Mandarin, Italian	35.00
Lemon, CA	9.50
Lemon, Argentina	12.50
Lemon, Italian	15.00
Lime, Mexican distilled	11.00

[a] Adapted from Chemical Market Reporter (1998).

Because of the small fruit size, the juice may not be recovered. However, juice recovered from the presses can be manufactured into a clarified juice product. The process involves clarifying by preservation with bisulfite, allowing cloud precipitation by pectinesterase, and traditional filtration with diatomaceous earth or by ultrafiltration. The clarified lime juice product is used in alcoholic drinks. Steam distillation of the oil occurs in a still with refluxing for 8–10 hr at pH of 2–2.5, with the oil recovered by decanting from the condensate. The refluxing is necessary to obtain the acid-catalyzed conversion of citral to p-cymene (and other changes) necessary to develop the unique flavor of the distilled lime oil. This conversion is reflected by lower aldehyde contents of the distilled oils presented in Table 11.4. The kinetics and compositional chemistry of these reactions has been thoroughly discussed in an excellent review (Clark and Chamblee, 1992). Even under rather mild temperature (37°C) stor-

TABLE 11.5 Properties of Cold-Pressed and Distilled Persian and West Indian Lime Oils

Property	Cold-Pressed		Distilled	
	Persian	W. Ind.	Persian	W. Ind.
Aldehydes (%)[a]	5.0	6.5	2.4	1.5
Specific gravity (20°C)	0.874	0.882	0.857	0.868
Refractive index (20°C)	1.483	1.483	1.475	1.477
Optical rotation (20°C)	+43.8	+37.5	+48.9	+46.0

[a] Expressed as citral (Kesterson et al., 1971).